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5th Int'l Hydrogen Peroxide Propulsion Conference
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(Statement A)

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Pressure Effects on Hydrogen Peroxide Decomposition Temperature

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Abstract

The use of very high concentration hydrogen peroxide (e.g., 98%) in rocket engines yields substantial specific impulse (Isp) gains when compared with traditional 90% peroxide engine systems. However, when used in pump-fed engines, 98% peroxide places a significant design burden on the turbine from a material strength and oxygen compatibility standpoint. The decomposition temperature for 98% peroxide is ~1240 K (~2230 R), a temperature regime in which most alloys show a precipitous decline in strength. Thus, accurate prediction of gas generator catalytic bed outlet temperature is necessary for confident life and structural margin assessment.

Analytical computations of maximum decomposition temperature at low pressures should be quite accurate using industry equilibrium chemistry codes such as the NASA/Lewis CEA computer program. Reported historical articles predict that ~50 K (~90 R) increase in temperature due to real gas effects could be expected at pressures of 20.7 Mpa (3000 psia) for 100% peroxide. A new analysis was performed to assess the validity of those estimates. The present calculations were made 1) using recent water and oxygen real gas properties with two classical mixing rules, and 2) using two equation-of-state methods with associated mixing rules. The new results indicate a real gas temperature effect of ~13 K (~23 R) at 20.7 Mpa (3000 psia). This smaller temperature increase should result in more manageable turbine design uncertainties.

Relevance of the Problem

Prior Pump-Fed Engine Operating Conditions

Pump-fed rocket engines using decomposed hydrogen peroxide as the turbine drive fluid have been demonstrated in flight vehicles. Historical examples include the German WWII V-2 and the British "Black Knight" (~1965). Both used peroxide in concentrations below 90%. The X-15 used 90% peroxide to drive the turbine on its LOX/ammonia engine. The turbine (Reference 1) operated at 2.6 Mpa (375 psia) and ~1011 K (~1820 R), and performed well as the engine demonstrated overall high reliability. Similarly, the Russians use peroxide as the turbine drive fluid on the Soyuz LOX/kerosene booster engines. The Soyuz has flown hundreds of successful missions over the last several decades. In the 1950's, Rocketdyne developed their aircraft rocket (AR) series of engines which were used to enhance the performance of jet fighter aircraft. The AR rockets accumulated a laudable record of operational capability and safety under field service conditions after its qualification in 1960. The AR2-3 used 90% peroxide as the oxidizer and the turbine drive fluid, and operated with turbine inlet conditions of 2.75 Mpa (400 psia) and ~1033 K (~1860 R). The turbine proved successful in the AR environment as an example of a high-concentration peroxide component designed for reusable service.

Advanced Pump-Fed Engine Configurations

Government and commercial industry have shown interest in a low toxicity replacement of storable toxic propellants (e.g., NTO and hydrazine class propellants) for space launch applications. Hydrogen peroxide has been identified as a potential oxidizer candidate. In order to be reasonably competitive with the Isp of the NTO and MMH (or hydrazine, 50-50, UDMH, etc.), high concentration peroxide must be considered. In the 1960's, a number of experimental programs investigated 98% peroxide catalyst, cooling, and thrust chamber technologies. However, no complete pump-fed engine systems were produced and flown.

Sparked by Air Force Space Maneuver Vehicle (SMV) rapid turnaround operability goals and NASA 2nd Generation Space Launch Initiatives (SLI), the analytical and experimental investigation of advanced pump-fed rocket engines using 98% peroxide has been rekindled. Initial uses have centered on upper stages with engines in the 10-20 Klb thrust range. All else being equal, the closed cycles have typically ~1-2% more specific impulse potential than the open cycles. The Air Force is exploring high performance alternatives to NTO/MMH. Thus, the closed cycles may align well with Air Force goals. NASA is pursuing cost reductions in upper stage operations. Therefore, the open cycles may satisfy NASA's low-cost objectives.

A typical open cycle gas generator operates at ~4.62Mpa (670 psia) and ~1228 K (~2210 R). When compared with 90% peroxide, turbines operating with 98% can be ~205 K (~370 R) hotter. In addition, pressures are much higher than in previous systems. A typical closed cycle preburner (gas generator) temperature is similar to that of the open cycle. However, the pressure is much higher (~16.5 Mpa [2400 psia]) due to the requirement that the turbine exhaust gas is fed into the main combustion chamber. The high pressure in the hot gas circuit is the primary disadvantage of closed cycle operation when compared with open cycles.

Turbine Design Implications

The combination of the higher temperatures and pressures when using 98% peroxide make the turbine design a more difficult challenge than in previous engine systems. The fundamental requirement is the identification of materials that are compatible with the pressure, temperature and oxygen concentration. New metallic alloys and advanced ceramic materials are the subject of research in the rocket and aircraft industries.

In addition to oxygen compatibility, the material for the turbine must exhibit sufficient strength. Two figures-of-merit (FOM) include the disk stress limit and the blade stress limit. Summarized in Table 1 are the typical design conditions for the open and closed cycles assuming a 98% peroxide engine inlet temperature of 300 K (540 R).

Table 1 Typical Turbine Design Conditions for Open and Closed Engine Cycles

Parameter	Open Cycle	Closed Cycle
Pressure, Mpa (psia)	4.83 (700)	17.2 (2500)
Gas Generator Temperature, K (R)	1234. K (2222)	1238 K(2229)
Relative Rotor Stagnation Temperature, K (R)	973 K (1751)	1179 K (2123)

Because the open cycle turbine operates at higher pressure ratio and at higher pitch velocity (to maximize turbine efficiency), the relative rotor stagnation temperature (the maximum temperature the rotor will usually attain) is lower as indicated in Table 1. From Reference 1, the implications on the disk stress limits are given in Figure 1. Placed on Figure 1 are the typical operating points for the open and closed cycles from Table 1. As shown, the high temperatures of 98% peroxide place turbine operation within the regime where typical material properties drop rapidly with temperature. When one operates within this "waterfall" region, small excursions in temperature can result in disproportionately larger changes in material stress margin. Interestingly enough, the open cycle relative disk stress margin may be similar to the closed cycle (depending on material selection) as shown in Figure 1. Because the blade stress parameter of both cycles is low for the applications studied, it is likely that somewhat more margin may exist for this stress parameter. In addition, the reduction in material strength will lower component fatigue life. The key point is that the elevated temperature of 98% peroxide places the turbine in a regime where small temperature uncertainty can be magnified into larger stress margin uncertainty.

Unlike bi-propellant gas generators (or preburners) the maximum temperature of peroxide decomposition is a function of only propellant enthalpy, concentration, and pressure. Mixture ratio streaking (due to injector effects) is not present. For the peroxide monopropellant, the only major upward temperature deviations result from real gas pressure effects since peroxide inlet enthalpy and concentration are measurable and predictable quantities. Previously reported real gas effects showed that a temperature increase of ~50 K (~90 R) might be expected at 20.7 Mpa (3000 psia). Referring back to Figure 1, such an increase could have noticeable impact on stress margin.

Historical Decomposition Temperature Estimates

Pressure effects on rocket grade peroxide (90-100% concentration) decomposition temperatures have been recently reported by General Kinetics (Reference 2) and are reproduced in Figure 2. The temperature trend at high concentrations (e.g., 98%) shows an increase of ~50 K (~90 R) at 20.7 Mpa (3000 psia). As expected, the trends are greater at lower concentrations due to both an increase in decomposition product water mole fraction and lower mixture temperature. The decomposition temperature of high concentration peroxide is well above the critical temperature of water which is 647.3 K (1165 R). Since the reported real gas effects appeared to be significant, the legacy of the reported data was researched.

The authors of the General Kinetics paper indicated that their data had been adapted from the FMC Hydrogen Peroxide Rocket Manual (Reference 3). The FMC curves corresponding to the General Kinetics curves are reproduced in Figure 3. It was noted that the FMC plots contained a reference to a Bureau of Mines report (Reference 4). The Bureau of Mines (BM) report was one of two volumes published in 1953 containing peroxide decomposition temperatures accounting for real gas mixture effects. Volume II (Reference 4) contained heterogeneous calculations while Volume I (Reference 5) contained homogeneous calculations. An excerpt of data from the BM heterogeneous report used in the FMC handbook is given in Figure 4.

Current Analyses

Evaluation of Bureau of Mines Data

Since the BM data is the genesis of some of today's reported maximum decomposition temperature trends, an examination of the data and the methods used to generate the data was performed. The BM assumed that the peroxide decomposition products were water and oxygen. According to equilibrium calculations (such as the NASA CEA code), trace product mole fractions are on the order of 10^{-4} or less at the temperatures of interest. Thus, the assumption of water and oxygen as the sole products of decomposition should be very good. The approach adopted by the BM was to use pure water and oxygen real gas data with special mixing rules to formulate the real gas mixture properties.

The mixing rules used by the BM were described by James Beattie in a 1949 Chemical Physics article. Those rules, given in Reference 6, include: 1) the General Limit Method, 2) Partial Volumes (Lewis and Randall Rule, also known as Amagat's Law), 3) Partial Pressures (Gibbs-Dalton Law). Unfortunately, the BM does not specify which mixing rule they selected. From the comparisons shown later in this paper, it could be inferred that the BM used Partial Pressures. The BM generated data for homogeneous mixtures (single phase) and for heterogeneous mixtures (allowing both liquid and gas phase water). The details of the approach referenced by the BM to compute liquid water concentrations were not pursued since, for the present applications of interest, the decomposition temperatures exceed the critical temperature of water.

For peroxide concentrations above ~75%, decomposition temperatures are above water's critical temperature. Thus, it would be expected that the BM results for the heterogeneous (Reference 4) and homogeneous (Reference 5) should be the same at high temperatures. The differences between the two calculations are given in Figure 5 for concentrations of 75% -100% and a pressure of 20.7 Mpa (3000 psia). Note that from 75-85% the differences are small (less than ~10 K), but that from 90-100% the differences jump significantly to ~40-100 K. The higher temperatures for the heterogeneous calculations could result from an assumption of a fraction of the water being in the liquid phase. However, the reasons for such a multi-phase composition for 90-100% peroxide decomposition products is not understood. Comparisons of the temperature departure from ideal for the BM heterogeneous and homogeneous data versus pressure and for 90-100% concentrations are given in Figure 6. For these concentrations, the BM heterogeneous temperatures significantly exceed the homogeneous values at all pressures. Based on Figures 5 & 6 and the analyses below, it would appear that the selection of the 90-100% BM heterogeneous data as a historical basis for real gas temperature estimates may have been an unfortunate choice.

Decomposition Temperature of Ideal Gases

Much of the real gas data in this paper is reported as temperature departures from the ideal gas state. This is done for two reasons: 1) the real gas temperature departures are small compared with the absolute temperature so plots of temperature would mask the departure effect; 2) various computer codes can show a variation as much as ~4 K in ideal temperature estimates. The latter is due to the source of the data base (e.g., date of JANNAF tables), the quality of the ideal gas property curve-fits, and finally the computational and print-out resolution. The basis for the ideal gas state of water and oxygen for this paper is the Third Edition of the Tables issued by JANNAF (Reference 7). Hydrogen peroxide thermodynamic properties (including the heat of

formation) can be found in Reference 3. The heat of formation for water/peroxide mixtures includes the heat of solution effect which at concentrations above 90% is small and often neglected in many rocket calculations. The ideal gas decomposition temperature for 100% liquid peroxide at 298.15 K (536.7 R) is 1275.1 K (2295.2 R). The 1996 NASA CEA program predictions closely agree with this value.

Decomposition Temperature of Real Gases

In order to clarify the real gas effects on peroxide decomposition temperature, the following approaches were taken to compute real gas temperatures: 1) two classical mixing rules using recent water and oxygen real gas properties; 2) two equation-of-state methods with associated mixing rules.

Following Beattie's methodology from Reference 6, the two mixing rules selected were: 1) Partial Volumes (Lewis and Randall Rule, also known as Amagat's Law), and 2) Partial Pressures (Gibbs-Dalton Law). Both require accurate real gas data for the pure fluids of interest (water and oxygen). The water data was derived from the NBS/NRC steam tables (Reference 8) while the oxygen data was compiled from the Russian Thermodynamic Properties of Oxygen report (Reference 9). Portions of the tabular data relevant to the pressures and temperatures of interest were extracted and incorporated into a computer program which automated the interpolation and iterative processes required by the recipes from Reference 6. According to Beattie, the two mixing rules often bracket real gas mixture behavior: "Up to moderate pressures the equilibrium pressure of a gas in a mixture computed from the Gibbs-Dalton law is too large. Since the Lewis and Randall rule gives too small a value for this quantity in the same pressure range, the true value lies somewhere between those given by these two assumptions, for gas mixtures."

An alternate calculation was made using BLAKE which is a computer code developed by the Army to predict properties of real combustion gas mixtures at high pressures. Versions of BLAKE implemented two equation-of-state methods: 1) truncated Virial; 2) NBS. The methods and their implementation in BLAKE are described in References 10 & 11. According to discussions with Freedman (Reference 11), the Virial method may yield less accurate results than the NBS method since the Virial method does not include the polar and asymmetric effects of the water molecule, while the NBS method attempts to incorporate such interactions. The motivation for using BLAKE was to broaden the analytical approaches in order to increase confidence in the computational results.

New Results

The partial pressure, partial volume and BLAKE (both Virial and NBS) methods were evaluated for peroxide concentrations of 90-100% and for pressures up to 20.7 Mpa (3000 psia), conditions most representative of rocket engine applications. In order to compare results with the BM data, initial enthalpy conditions for the constant enthalpy decomposition process were assumed to be 291.5 K (524.7 R) and one atmosphere. For a real process, pumping the peroxide to high pressure slightly increases the peroxide temperature (and enthalpy) which will result in an increased decomposition temperature. However, the effects are usually small (~5 K) and will not be included in the present analyses. Parametric results of the current analyses are given in Figures 7-10 where the departures from ideal gas behavior are plotted.

In Figure 7, the BM homogeneous calculations are compared with the current Partial Volume and Partial Pressure computations. The BM heterogeneous data were not considered due to the previously described irregularities. As seen in Figure 7, the BM homogeneous curves closely follow the current curves for the Partial Pressure method. It might be inferred that the BM used the Partial Pressure method as their gas mixture approach. As expected, the Partial Volume and Partial Pressure methods show differences, with the Partial Volume method being higher than the Partial Pressure method. However, the differences are not large, being only ~ 9 K (~ 16 R) at the worst case examined (20.7 Mpa [3000 psia] and 90% peroxide).

In Figure 8, the BLAKE Virial calculations are compared with the current Partial Volume and Partial Pressure computations. The Virial data falls consistently just below the Partial Pressure method. In Figure 9, the BLAKE NBS calculations are compared with the current Partial Volume and Partial Pressure computations. The NBS data falls consistently between the Partial Volume and Partial Pressure methods. This suggests that the BLAKE NBS method may be more representative than the Virial method for water/oxygen system, based on the expectations of Beattie (Reference 6) that the real gas mixture properties would likely be bounded by the Partial Volume and Partial Pressure approaches.

Advanced peroxide rocket engine systems under consideration today have baselined 98% peroxide concentration. Figure 10 shows the temperature departures for 98% peroxide using the Partial Volume, Partial Pressure, and BLAKE NBS methods. The spread from the different methods at 20.7 Mpa (3000 psia) is only ~ 4 K. If one were to select a worst case method (i.e., highest temperature departure), the Partial Volume data could be used. The BLAKE NBS data might be selected as representative, as it falls between the Partial Volume and Partial Pressure methods. Referring to Figure 10, it can be seen that the expected temperature departure for typical closed cycle engine conditions (pressure ~ 16.5 Mpa [2400 psia]) is ~ 11 K (~ 20 R). This is significantly below the 45-50 K (80-90 R) that was reported in References 2-4. The reduction in maximum expected temperature should make the task for the turbine designer somewhat easier from a stress and fatigue standpoint. In Figure 11, the absolute decomposition temperature for 98% peroxide is given as a function of pressure with the assumption of an initial peroxide temperature of ~ 304 K (~ 547 R). Although the current temperature departures from ideal are small, a carefully conducted experiment could be performed to confirm the analytical predictions.

Conclusions

Advanced pump-fed rocket engines using high concentration peroxide (e.g., 98%) operate with turbine inlet temperatures above 1225 K (2205 R). At these temperatures, materials for the uncooled turbine components show precipitous decline in mechanical performance (strength and fatigue life). Several literature sources cite pressure effects on peroxide decomposition temperature. Those sources showed an increase in temperature with pressure, approaching 50 K (90 R) at 20.7 Mpa (3000 psia) for 100% peroxide. Research of the genesis of the trends traced the data to a 1953 Bureau of Mines report. New analysis indicates that the Bureau of Mines data were inaccurate and that the non-ideal pressure effects on temperature are much lower.

Four analytical gas mixing methods were used to compute the temperature departure effects of pressure on a real gas mixture: 1) Partial Pressures, 2) Partial Volumes, 3) Truncated Virial

(BLAKE code), 4) NBS Equation-of-State (BLAKE code). The four methods gave answers spanning less than 5 K at 20.7 Mpa (3000 psia) with 100% peroxide. A mean estimate at 20.7 Mpa (3000 psia) for 100% peroxide is ~13 K (~ 23 R) higher than ideal. In the absence of corroborating experimental data, the Partial Volume method could be used to set the upper bound, while the NBS (BLAKE) method may give a representative mean value. The significantly reduced real gas temperature departure effects should translate into greater confidence in turbine component design.

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Figure 1 Turbine Blade Stress Limits

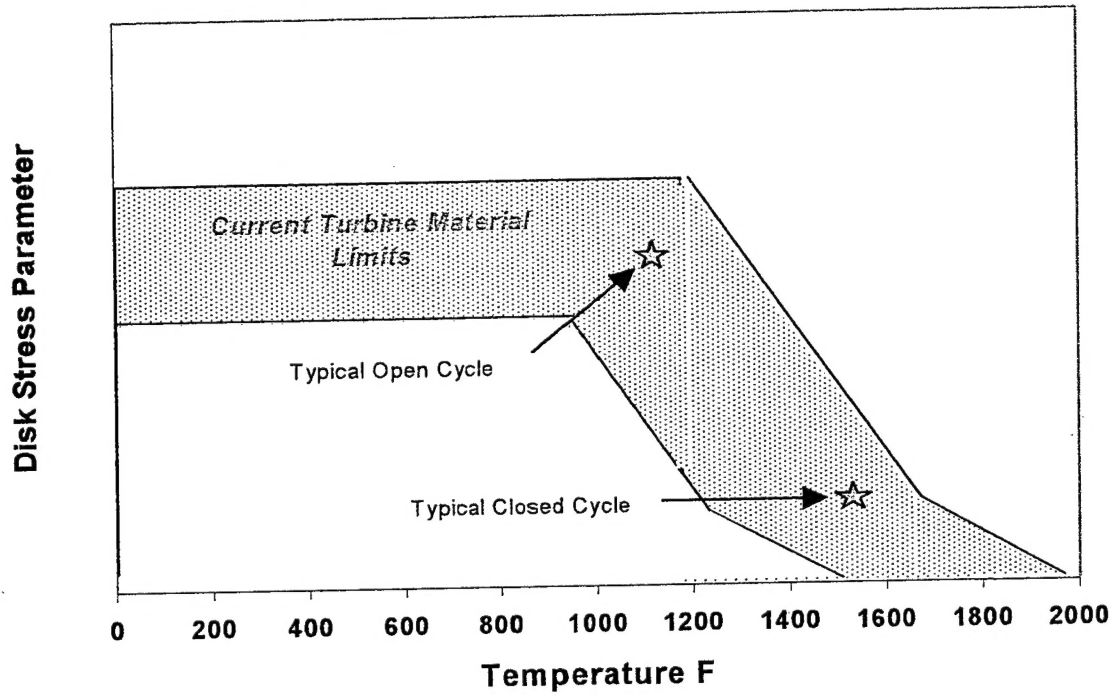


Figure 2 Pressure Effects on Decomposition Temperature From Reference 2

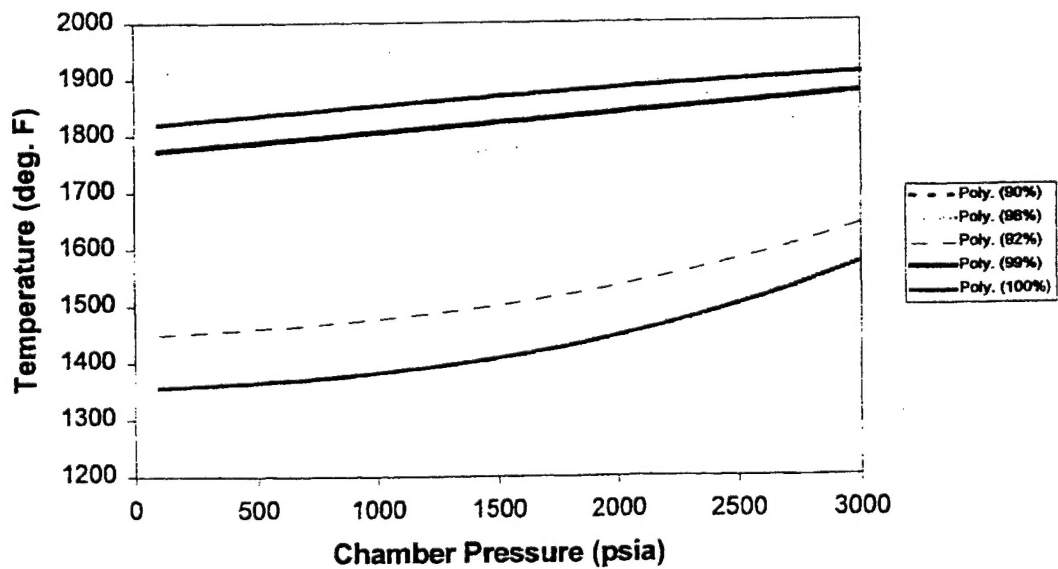


Figure 3 Pressure Effects on Decomposition Temperature From Reference 3

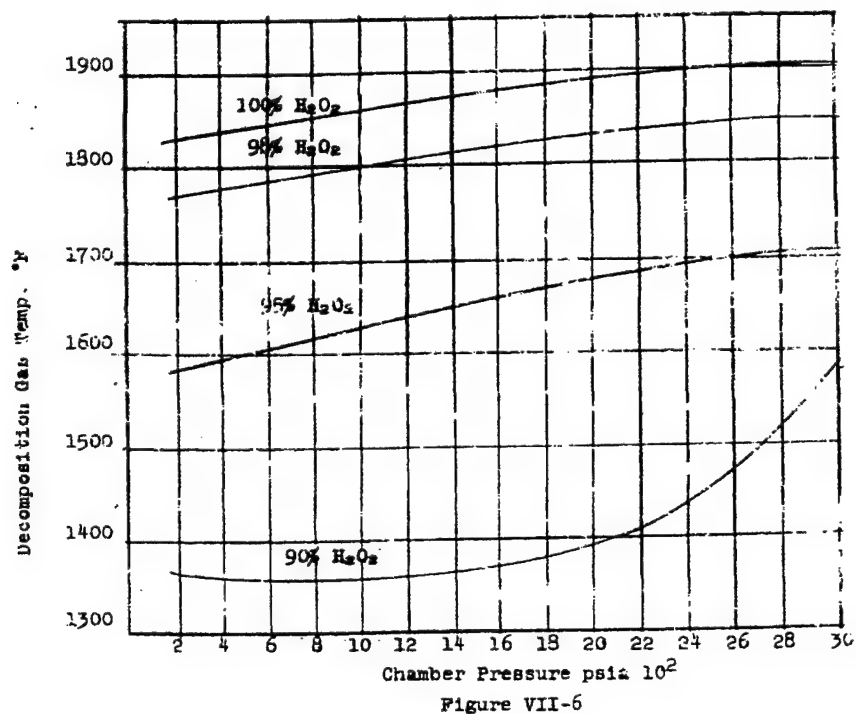
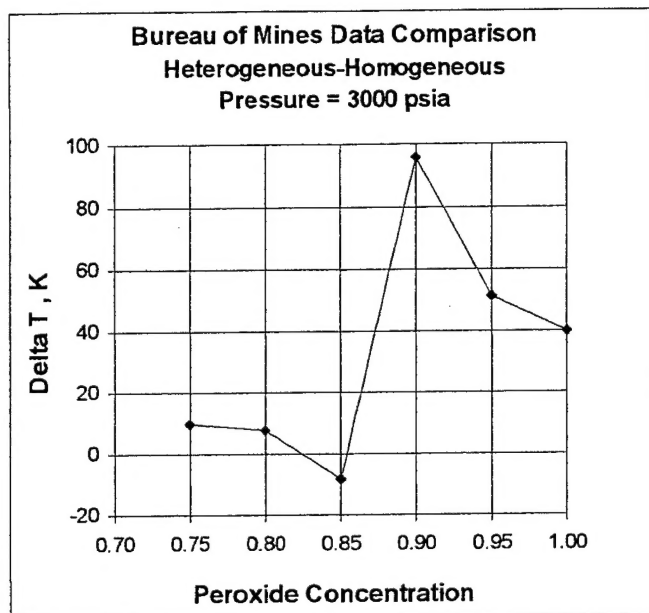


Figure 4 Pressure Effects on Decomposition Temperature From Reference 4

TABLE 1. - Thermodynamic properties of the decomposition products of hydrogen peroxide systems at flame temperatures (cont'd)

R	P (psia)	T _f (°K)	h (cal/gm.)	q (cal/deg. gm.)	ρ (gm./cm ³)
1.00	100	1267	-1203.0	2.4780	0.0001483
	150	1268	-1203.0	2.4426	.0002223
	200	1269	-1203.0	2.4176	.0002962
	250	1270	-1203.0	2.3982	.0003700
	300	1271	-1203.0	2.3825	.0004437
	350	1272	-1203.0	2.3691	.0005172
	400	1273	-1203.0	2.3576	.0005906
	450	1274	-1203.0	2.3475	.0006639
1.00	500	1275	-1203.0	2.3384	0.0007371
	600	1277	-1203.0	2.3229	.0008832
	700	1279	-1203.0	2.3096	.0010289
	800	1281	-1203.0	2.2983	.0011741
	900	1283	-1203.0	2.2883	.0013190
	1000	1285	-1203.0	2.2794	.0014634
	1100	1287	-1203.0	2.2713	.0016075
1.00	1200	1289	-1203.0	2.2640	0.0017513
	1300	1290	-1203.0	2.2573	.0018946
	1400	1292	-1203.0	2.2511	.0020376
	1500	1294	-1203.0	2.2454	.0021803
	2000	1302	-1203.0	2.2315	.0028892
	2500	1309	-1203.0	2.2030	.0035911
	3000	1316	-1203.0	2.1879	0.0042872

**Figure 5 Comparison of Heterogeneous and Homogeneous Peroxide Decomposition Temperature Differences From Bureau of Mines (References 4 & 5)
At 20.7 Mpa (3000 psia)**



**Figure 6 Comparison of Heterogeneous and Homogeneous Peroxide Decomposition Temperatures From Bureau of Mines (References 4 & 5)
For 90-100% Peroxide Concentrations**

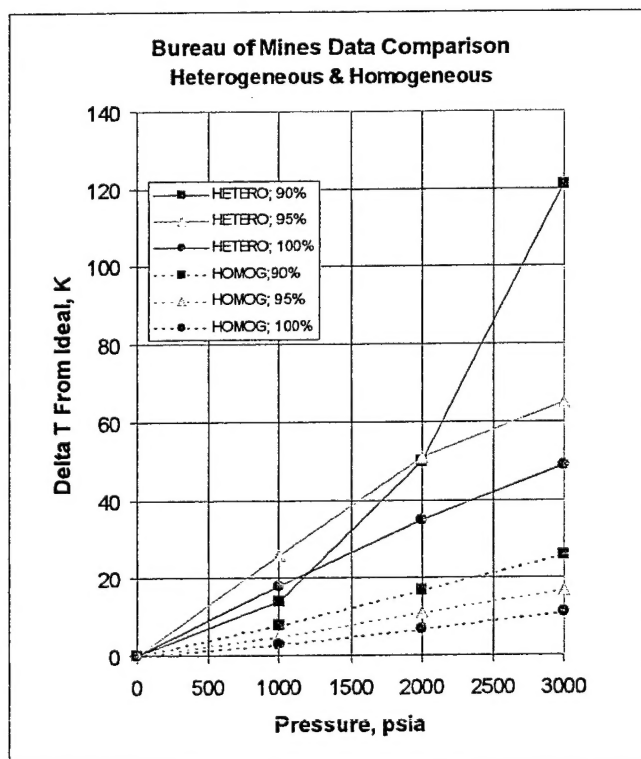


Figure 7 Temperature Departure Comparison: BM Homogeneous With Partial Pressure and Partial Volume Methods

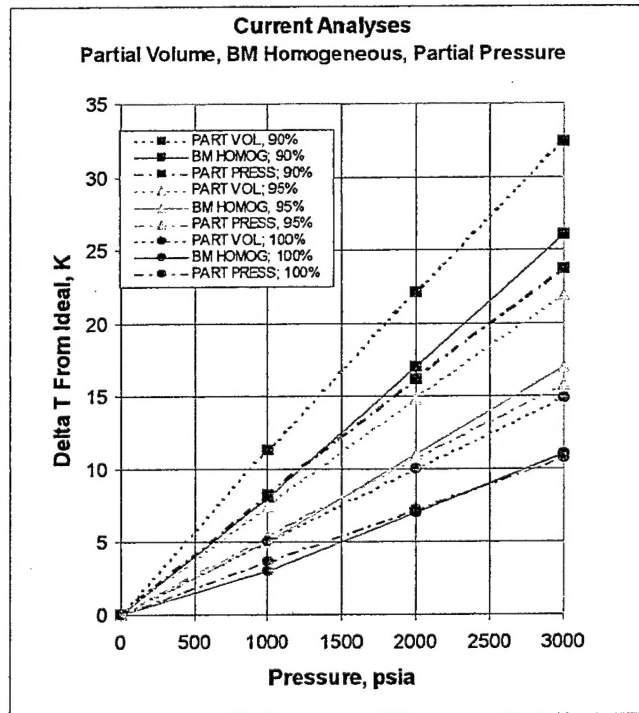


Figure 8 Temperature Departure Comparison: Blake Virial With Partial Pressure and Partial Volume Methods

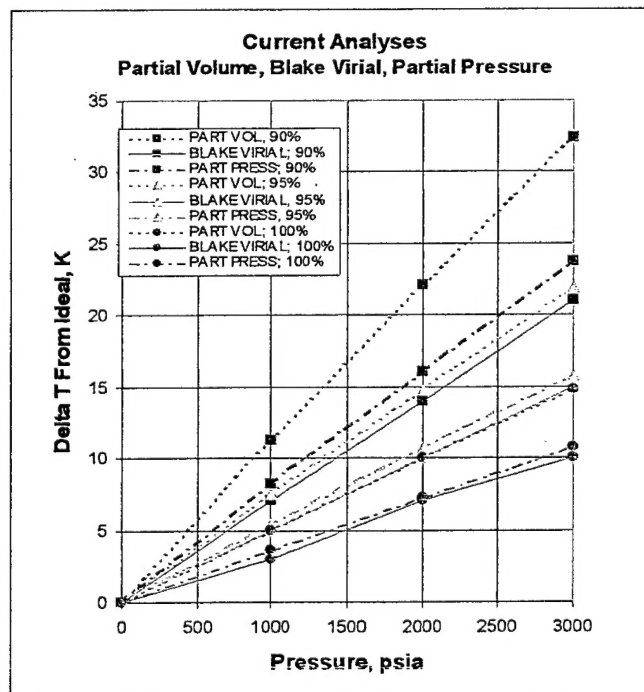


Figure 9 Temperature Departure Comparison: Blake NBS With Partial Pressure and Partial Volume Methods

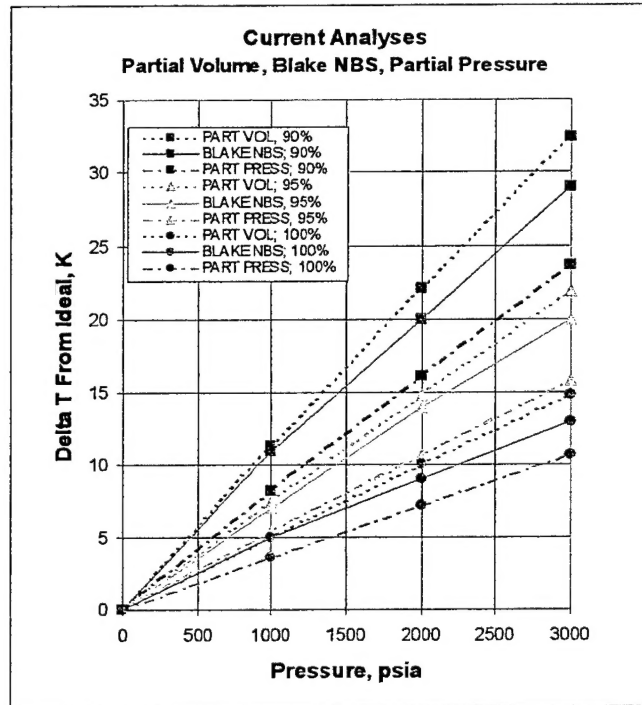
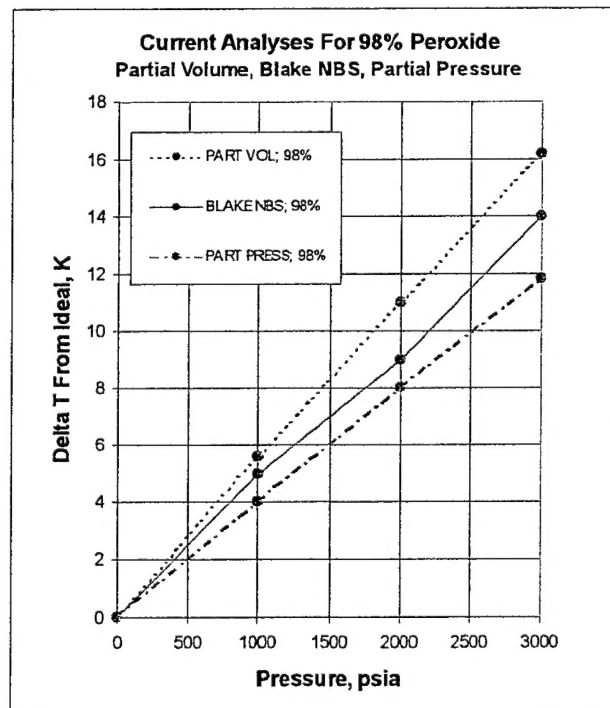


Figure 10 Temperature Departure Comparison: Blake NBS With Partial Pressure and Partial Volume Methods for 98% Peroxide



**Figure 11 Absolute Temperature Using Blake NBS For 98% Peroxide
(Initial Temperature ~ 304 K)**

